HYDROUS PYROLYSIS OF NEW ALBANY AND PHOPHORIA ᴊHALES: EFFECTS OF TEMPERATURE AND PRESSURE ON THE KINETICS OF PRODUCTION OF CARBOXYLIC ACIDS AND LIGHT HYDROCARBONS

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ABSTRACT

We used hydrous pyrolysis to determine the production kinetics of carboxylic acids and light hydrocarbons over the temperature interval 200° to 330°C at 300 and 600 bar pressure. We used Dickson-type, gold-bag autoclaves (1) allowing us to acquire multiple fluid and gas samples under *in situ* conditions throughout the runs, each lasting from 60 to 120 days, depending on temperature. During the runs and while sampling, fluids were exposed to only non-reactive materials (gold, passivated titanium and glass gas-tight syringes). Gases were extracted into He and analyzed using GC and MS. The aqueous samples were analyzed for carboxylic acids using IC, for inorganic cations using ICP-ES and for inorganic anions using IC. Carbon disulfide extractions were made on some aqueous fluids allowing GC analyses for heavier hydrocarbons.

The kerogen pyrolysis produced significant amounts of the monocarboxylic acids (acetic > propionic > butyric). Formic acid was present only briefly at the start of runs and little, if any, of the dicarboxylic acids were produced. The gases were dominated by CO_2 and methane, in that order, and progressively smaller amounts of the alkanes (ethane > propane > butane > pentane). Preliminary kinetic analyses of production rates suggest activation energies (E) ranging from 50 to 60 kcal/mol for both the light hydrocarbons and acids. Pressure had little effect on measured rates for the New Albany Shale.

INTRODUCTION

The potential importance of the carboxylic acids in generating reservoir porosity and controlling aqueous fluid chemistry (2) has resulted in considerable interest in knowing their rate of production and thermal stability (3), although not without some controversy (4). The recognition of the reactivity of organic compounds in aqueous solutions at high temperature (5) has argued for the use of hydrous pyrolysis as a particularly appropriate method of investigation (6). Unfortunately, experimental artifacts, like catalysis by the reaction vessel (6), and inappropriate kinetic analyses (7) have sometimes conspired to complicate progress in understanding the processes and rates.

We are studying the pyrolysis of oil shales and the generation of carboxylic acids and light hydrocarbons using chemically inert (Au and Ti) hydrothermal reaction vessels specifically designed to allow sampling of fluids under *in situ* condi-

tions. In this way we hope to avoid many of the complications noted by others. In addition, we are using a variety of approaches to kinetic analyses in determining kinetic parameters.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

The term hydrous pyrolysis has been used by some workers (8) to mean a relatively specific, restrictive experimental approach. Although useful for comparison between samples of the "potential for generating oil-like pyrolysate", this approach may not be ideally suited to studies aimed at mechanisms and kinetics of processes. We use the term more loosely to imply simply the pyrolysis (cracking) of kerogen in the presence of liquid water. Our lowest pressure (300 bar) was sufficiently high to keep the aqueous system single phase throughout each run. The use of a flexible gold bag allows us to control pressure (e.g., isobaric) through significant degrees of maturation. This approach has been used to advantage by others (9). Our apparatus differs from that of these earlier workers, however, in that we may withdraw multiple samples from each run while maturation continues uninterrupted. Concentration *vs.* time data are adjusted to compensate for the change in area/mass ratio caused by sampling.

Runs were isothermal (after a heating period lasting a few hours) and isobaric. All runs used 30 g of shale and an appropriate volume of de-oxygenated (purged using N_2 gas) distilled water to just fill the gold bag at run conditions. The headspace was further swept with N_2 gas prior to collapsing the gold bag before heating and pressurizing the vessel. Each run lasted from 2 to 4 months, depending on temperature. At the highest temperature, this allowed us to follow both the production and subsequent destruction (through decarboxylation) of the organic acids. A total of five runs were made with the New Albany Shale: 200°, 270° and 330°C at 300 bars pressure, 270° at 500 bars pressure, and 330°C at 600 bars pressure. Two runs are still in progress with the Phosphoria Shale at 330°C at 300 and 600 bars pressure. The Phosphoria Shale runs will not be dealt with here.

The shale samples were coarsely crushed (2 to 4 mm) and then washed ultrasonically in distilled water to remove adhering fine particles. We were faced with the usual conundrum of deciding whether or not to pre-extract the samples prior to hydrous pyrolysis. If we pre-extracted, we ran the risk of performing the hydrous pyrolysis on material unrepresentative of natural kerogen. If we didn't pre-extract, we would need to account for any light hydrocarbons or carboxylic acids released immediately upon heating that were the product of natural maturation and not the artificial maturation taking place as a result of the hydrous pyrolysis. We elected not to pre-extract, because we felt that the water washing would remove some of the acids already present, and because we could correct for the initial acid input, since we would take closely spaced samples early in each run.

During the runs and while sampling, fluids were exposed to only non-reactive materials (gold, passivated titanium and glass gas-tight syringes). Gases were extracted into He and analyzed using GC and MS. The aqueous samples were analyzed for carboxylic acids using IC, for inorganic cations using ICP-ES and for inorganic anions using IC. Carbon disulfide extractions were made on some aqueous fluids allowing GC analyses for heavier hydrocarbons. At the conclusion of each run the vessels were quenched to room temperature and pressure and the solids and remaining liquids recovered and sampled. Although the gas and liquid analyses are essentially complete for the five runs, the solid phase analyses continue. These will include XRD, SEM/electron microprobe, and pyrolysis-MS analyses.

Initial TOC analyses made post-run suggest that significant degrees of artificial maturation were achieved. For example, the 270°C and 300 bar run achieved 30% conversion (based on kerogen loss) during the two months of artificial maturation.

RESULTS

Carboxylic acids

The kerogen pyrolysis produced significant amounts of the monocarboxylic acids (acetic > propionic > butyric). Formic acid was present only briefly at the start of runs. No dicarboxylic acid anions were unequivocally identified in any samples, suggesting that if they are produced at all under any of the conditions that we investigated, their production rate is very small. Figure 1 illustrates typical results for the carboxylic acids produced at 270°C. Note that at all temperatures there was an initial rapid release of carboxylic acid anions to the aqueous phase upon heating. In the subsequent kinetic analyses we have corrected the results for this initial pulse of released carboxylic acid. At 270°C, following the initial pulse, carboxylic acid concentrations continue to increase throughout the runs.

Figure 2 illustrates typical results for the carboxylic acids produced at 330°C. At this temperature the production rate of the carboxylic acids is much higher than at 270°C, however, within a few days the rates of production and destruction via decarboxylation are about equal. Within two weeks the rate of decarboxylation exceeds the rate of production and there is a continuous decrease in carboxylic acid concentration throughout the remainder of the runs. It is very likely that both the processes of production and decarboxylation are catalyzed by the mineral phases in the shale and, although our experimental apparatus is unlikely to have catalyzed processes, any rates that we measure are specific to these shales.

Light hydrocarbons

Unlike the carboxylic acids, the light hydrocarbons (<C7) and CO_2 were not rapidly released upon initial heating in water, implying that such compounds produced as a result of natural maturation are rapidly lost from the kerogen. The gases were dominated by CO_2 and methane, in that order, and progressively smaller amounts of the alkanes (ethane > propane > butane > pentane). Figure 3 illustrates typical results for these compounds at 270°C. Gas concentration continues to increase throughout the runs.

Effect of pressure

Pressure (300 vs. 600 bars) had little effect on the production of either the carboxylic acids or the light hydrocarbons produced from the pyrolysis of kerogen contained in the New Albany Shale. As an illustration, Figure 4 compares the 330°C carboxylic acid results obtained at the two pressures.

KINETIC ANALYSES

The concentration data were used to calculate fraction reacted on an absolute scale, based on the maximum concentration measured for each compound during the period of production. We then used the KINETICS code (10) to analyze the data acquired from the hydrous pyrolysis experiments. Table 1 summarizes the kinetic analyses.

For the gases, the data acquired at all three temperatures were used in the kinetic analyses. At 200°C over a 4 month period, little if any carboxylic acid was

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produced by the artificial maturation. All of the carboxylic acid present at this temperature was that produced naturally and rapidly released to the aqueous phase upon heating. For this reason, the kinetic analyses of the carboxylic acid data are based only on the results from the 270° and 330°C runs.

In order to test our assumption that the reactions producing the carboxylic acids and light hydrocarbons were first order, we first made a kinetic analysis based on a Gaussian distribution of activation energies with all terms (the pre-exponential (A), activation energy (E), Gaussian distribution parameter (S), and reaction order (N)) calculated by fit, rather than being fixed. The mean calculated N for the gases was 0.98 ± 0.12 and for the carboxylic acids was 0.87 ± 0.10. The results suggested that for all compounds the production reaction may be assumed to be approximately first order, although a spread in calculated activation energies resulted from the sparseness of the data. Pyrolysis kinetics determined using a Pyromat II instrument suggested that an appropriate pre-exponential factor, A, for the production of volatile hydrocarbons from the New Albany Shale was 2×10^{14} (11). The kinetics analyses summarized in Table 1 used this value.

The kinetic analyses suggest that the activation energies for the production of both the light hydrocarbons and the carboxylic acids from the hydrous pyrolysis of kerogen contained in the New Albany Shale are within the range of 50 to 60 kcal/mole.

CONCLUSION

We have demonstrated the use of a new type of hydrothermal apparatus in determining the production kinetics of light hydrocarbons and carboxylic acids from kerogen pyrolysis. It is ideally suited to determine the effects of temperature and pressure on production kinetics, free of the experimental artifacts frequently encountered using other types of apparatus.

In this paper we have only presented preliminary results from the organic analyses of fluids and gases. We are continuing to analyze the data from solid phase analyses and from the inorganic fluid chemistry analyses. We intend to try to understand the interaction between the inorganic and organic chemical systems. We are especially interested in the effectiveness of carboxylic acids in complexing the cations released as a result of mineral dissolution, i.e., the increase in "solubility", and the impact of the carboxylic acids on the solution pH. We are utilizing the geochemical modeling code EQ3/6 (12) in this effort.

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TABLE 1

KINETIC ANALYSES OF PRODUCTION RATE DATA

Compound	Pressure (bar)	E (kcal/mol)	A (s^{-1})	S (%E)	N
methane	300	55.3	2e14	3.46	1
	600	55.2	"	3.06	"
ethane	300	55.1	"	3.73	"
	600	54.9	"	1.71	"
propane	300	55.6	"	4.16	"
	600	54.9	"	0.57	"
butane	300	55.5	"	4.25	"
	600	55.7	"	1.49	"
acetate	300	52.6	"	0.77	"
	600	52.6	"	0.84	"
propionate	300	52.5	"	1.44	"
	600	51.6	"	2.49	"
butyrate	300	52.9	"	0.09	"

Figure 1. NA-1 (270°C, 300 bar)
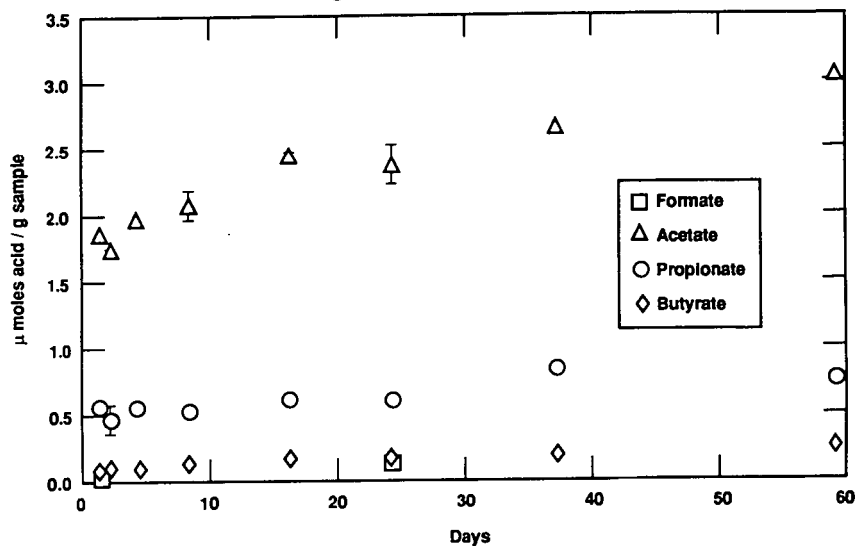
Figure 2. NA-7 (330°C, 600 bar)

ES-05/28/92-KK#4-01 & 02
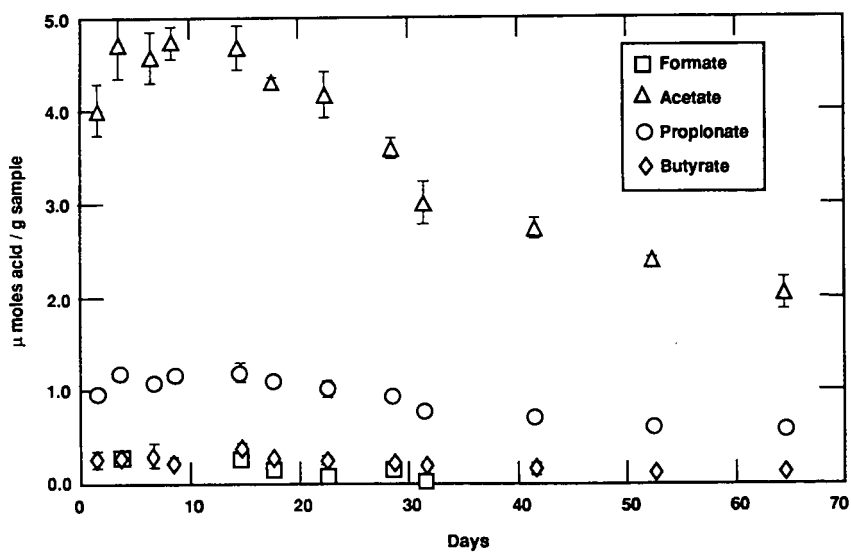
Figure 3. NA-4 gasses (270°C, 500 bar)
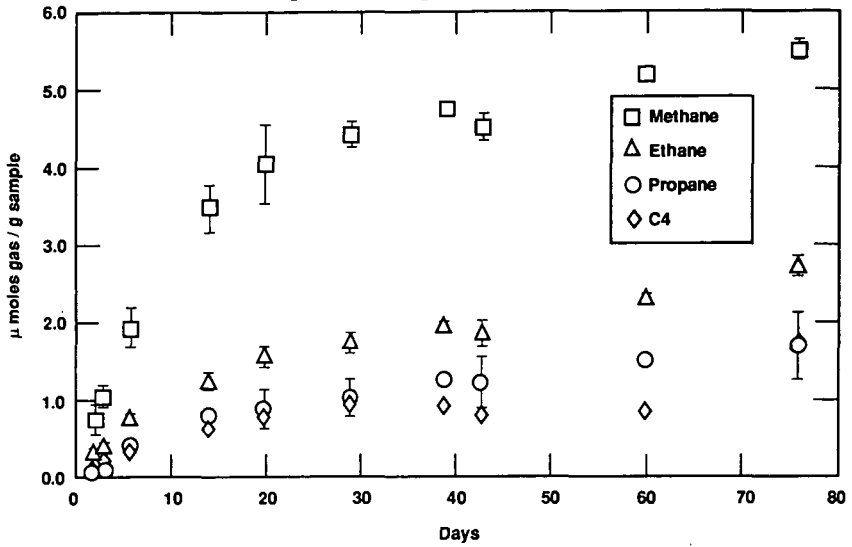
- □ Methane
- △ Ethane
- ○ Propane
- ◇ C4

Figure 4. New Albany Shale at (330°C and 300 or 600 bar)

- △ Acetate
- ○ Propionate
- ▲ Acetate
- ● Propionate

open = 300 bar
closed = 600 bar

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